ARSENIC SEPARATION FROM SEA WATER BY FLOTATION AND DETERMINATION BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY FOLLOWING ARSINE GENERATION

Susumu NAKASHIMA

It is important to develop a rapid and accurate method of determining arsenic(III, V) in sea water for certain marine biology, oceanography and environmental chemistry assays. Arsenic probably exists at the 1–4 $\mu g\ l^{-1}$ level, mainly as arsenate, in natural sea water (1–4). At such low concentrations a precise direct determination is impracticable even by atomic-absorption spectrophotometry of arsine, which has high sensitivity (5–8). Accordingly, arsenic must be concentrated from sea water prior to determination.

Coprecipitation with iron(III) hydroxide (9) is commonly used as a preconcentration technique for determination of arsenic in water. This bulky amorphous precipitate, however, is difficult to filter, and larger volumes are cumbersome to centrifuge.

In a previous paper (10), flotation technique (11, 12) was used to separate sub-microgram amounts of arsenic(III, V) coprecipitated with iron(III) hydroxide from natural non-saline waters with the subsequent determination of arsenic content by generation of arsine using sodium borohydride ($NaBH_4$) as a reductant and atomic-absorption spectrophotometry with a long absorption tube (60 × 1.2 cm i.d.).

This paper describes an application of this separation-determination method with suitable modifications, to analysis of arsenic in sea water.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash, Model AA-1 Mark II, atomic-absorption spectrophotometer equipped with a Westinghouse arsenic hollow-cathode lamp and a custom-made silica absorption cell (60 × 1.2 cm i.d.) was used with a Beckman burner supplied with nitrogen and hydrogen.

The apparatus used for hydride generation was a modified Nippon Jarrell-Ash, Model ASD-1A, arsenic measurement unit coupled to a custom-made hydride generating cell approximately 40 ml in volume. A schematic diagram of the analytical system is illustrated in Fig. 1.

All pH readings were made with a Hitachi-Horiba, Model M-5, pH meter together with a combined glass electrode.

The flotation and separation apparatus was similar to that described by Mizuike and co-workers (11, 12). The flotation cells used were glass cylinders, "A" (40 × 6.5 cm i.d.) and "B" (24 × 4.8 cm i.d.), which were fitted with a

sintered-glass filter (No. 4) to generate small bubbles. The design of the flotation cell is shown in Fig. 2.

The air that served as inert gas was supplied by a Nippon Jarrell-Ash, Model AMD-B1, air pump unit.

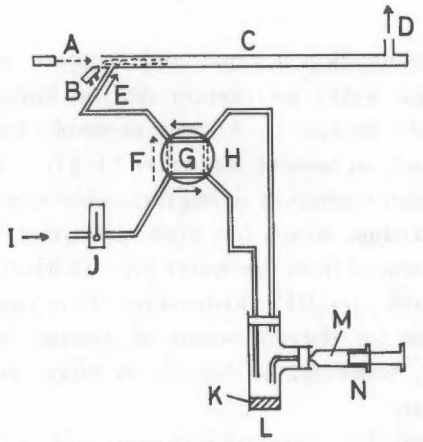

Fig. 1. Schematic diagram of analytical system. A, Light from arsenic hollow-cathode lamp; B, Beckman burner; C, silica absorption tube (60 × 1.2 cm i.d.); D, outlet from tube; E, nitrogen gas-flow containing arsine; F, bypass; G, four-way stopcock, alternative gas passages shown by broken lines; H, gas-flow with valve in sweep position; I, nitrogen supply; J, flow meter; K, sodium borohydride solution; L, arsine generating cell; M, sample solution; and N, syringe.

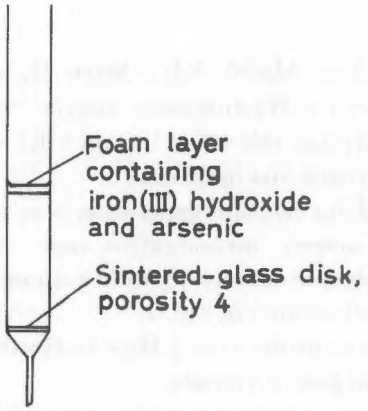

Fig. 2. Flotation cell for pre-concentration of arsenic.

Reagents

All reagents were of analytical reagent grade, except for sodium oleate and sodium lauryl sulfate. Aqueous reagents were prepared in de-ionized, distilled water. Stock solutions (1 mg ml^{-1}) of As(III) and As(V) were prepared from diarsenic trioxide (As_2O_3) and sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), respectively, and arsenic standard solutions were freshly prepared by diluting stock solutions before use. An iron(III) solution (5 mg ml^{-1}) was prepared from ammonium iron(III) sulfate [$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$]. A sodium oleate solution (1 mg ml^{-1}) was prepared by dissolving sodium oleate (powder, extra-pure reagent, Wako Pure Chemicals, Osaka) in 99.5 v/v % ethanol with magnetic stirring. A sodium lauryl sulfate solution (1 mg ml^{-1}) was prepared by dissolving sodium lauryl sulfate (powder, extra-pure reagent, Wako Pure Chemicals) in 99.5 v/v % ethanol. A potassium iodide solution (20 w/v %) was prepared by dissolving powder in water. A sodium borohydride solution (5 w/v %) was used in 0.1 M sodium hydroxide solution.

Separation of arsenic from sea water

A sea water sample of 250 m*l* was placed in a 300-m*l* beaker and 2 m*l* of iron(III) solution added. The pH was adjusted to 8–9 with aqueous ammonia solution (5 and 0.1 M) in order to precipitate iron(III) hydroxide, by stirring magnetically for 15 min. Sodium oleate solution (1 m*l*) was added into the beaker. The beaker contents (excluding the stirring bar) was transferred to flotation cell "B", and residue in the beaker washed into the cell using two small portions of water. Air was passed at a flow-rate of 50 m*l* min^{-1} from the lower end of the cell for about 1 min, to obtain complete mixing and flotation of the precipitate. The mother liquor was sucked through the sintered-glass disk and the precipitate washed with 30 m*l* of water. Four milliliters of 5 M hydrochloric acid was added to the cell to dissolve the precipitate; the filtrate collected by suction in a 10-m*l* calibrated flask, the sintered-glass disk washed with hydrochloric acid; and the washings added to the flask and diluted to 9 m*l* with 5 M hydrochloric acid. Potassium iodide solution (0.5 m*l*) was added into the flask prior to analysis and diluted to the mark with water.

Analysis of arsenic

Freshly prepared 5 w/v % sodium borohydride solution (1 m*l*) was transferred into an arsine-generating cell, and the cell attached to the apparatus. The needle of the plastic syringe with 1 m*l* of sample solution containing less than 0.10 μg of arsenic was inserted through the side-arm seal of the cell. The four-way stopcock of the apparatus was turned to the sweep position to introduce nitrogen into the system, and the sample injected into the cell. The arsine thus generated was swept into the long absorption cell with nitrogen so that it was atomized in the nitrogen-hydrogen flame and the absorption signal marked on the recorder. The stopcock was returned to the by-pass position. The cell was

carefully rinsed with distilled water and recharged with sodium borohydride solution for the next sample. If the concentration of arsenic exceeded 0.10 μg ml^{-1}, the solution was diluted further by adjusting the hydrochloric acid, iron (III) and potassium iodide concentrations accordingly.

A calibration curve was obtained using 4.5 M hydrochloric acid solutions containing 1 mg ml^{-1} iron(III), 1 % potassium iodide and 0–0.10 μg ml^{-1} arsenic(III). The calibration curve for arsenic was linear up to 0.10 μg ml^{-1} of arsenic.

The atomic-absorption equipment was operated under the following conditions: wavelength, 193.7 nm; lamp current, 14 mA; gas flow-rates, nitrogen 1.5, hydrogen 1.5 and auxiliary nitrogen 6 l min^{-1}; slit (spectral band width), 1 nm.

The arsenic in a sample solution was also determined by atomic-absorption spectrophotometry using an arsine generation-electrically heated silica tube (tube size, 30 × 1.2 cm i.d.; tube temperature, 900 ℃; nitrogen flow-rate, 1l min^{-1}). A schematic diagram of the apparatus is shown in Fig. 3.

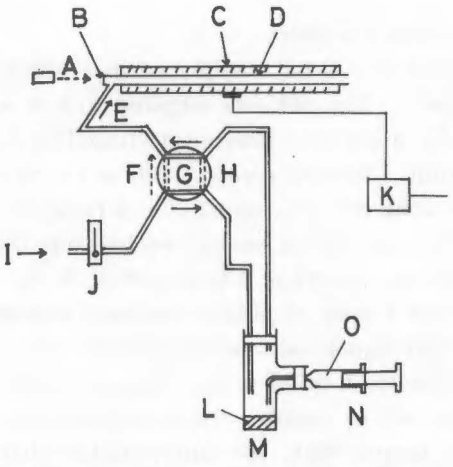

Fig. 3. Schematic diagram of analytical system using furnace tube. A, Light from arsenic hollow-cathode lamp; B, silica window; C, electric furnace; D, silica absorption tube (30 × 1.2 cm i.d.); E, nitrogen gas-flow containing arsine; F, bypass; G, four-way stopcock, alternative gas passages shown by broken lines; H, gas-flow with valve in sweep position; I, nitrogen supply; J, flow meter; K, temperature controller; L, sodium borohydride solution; M, arsine generating cell; N, syringe; and O, sample solution.

RESULTS AND DISCUSSION

A water sample of 250 ml was considered a suitable volume, taking into consideration the arsenic content (average, 2 μg l^{-1} level) in natural sea water and the sensitivity of the analytical equipment.

In sea water samples, a surfactant solution was added just before flotation for complete separation of precipitate.

Initially, various parameters, such as pH, amounts of iron(III) and sur-

factant added and effects of stirring time, were tested using 250 m*l* of artificial sea water prepared by the Lyman and Fleming (13) formula to determine the optimum conditions for flotation and determination of the arsenic.

The pH effect was examined on coprecipitation of arsenic with 250 m*l* of artificial sea water containing 0.5 μg of arsenic(III, V), 10 mg of iron(III) and 1.0 mg of sodium oleate. Hydrochloric acid solution and aqueous ammonia solution were used to adjust the pH value to within the range 3.5–9.5. Over this range, satisfactory recoveries were obtained for both trivalent and pentavalent states of arsenic. The most stable layer of surface foam supporting the precipitate of iron(III) hydroxide was formed within the pH range 7–9.5; thus, pH range of 8 – 9 was used throughout this work.

At pH below about 6.5, a stable surface-foam layer was obtained by using sodium lauryl sulfate as surfactant.

Satisfactory recovery of the test sample of arsenic(III) was obtained with 2.5–20 mg iron(III) under stirring for 5–40 min and with 0.5–6 mg of surfactant. In practice, the operating conditions described in the experimental section were used.

Artificial sea water solutions (250 m*l*) at pH 8–9 containing 10 mg of iron (III), 1.0 mg of sodium oleate and arsenic(III, V) at 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 8.0, 10.0, 15.0, or 20.0 μg were analyzed by the proposed procedure. Recovery of the test arsenic was greater than 95 % in all instances. The proposed conditions, therefore, appear to be optimum for 250–m*l* volumes of artificial sea water containing up to 20 μg of arsenic.

In this study, potassium iodide was added after flotation. Table 1 compares permissible amounts of foreign ions with and without potassium iodide in determinations of 0.5 μg of arsenic(III) in 500 m*l* solution with 10 mg of added iron (III), using flotation cell "A". Yamamoto *et al.* (6, 14) reported that the addition of potassium iodide to the sodium borohydride tablet reduction system using

TABLE 1

Comparisons of permissible amounts of foreign ions in determinations of arsenic with and without potassium iodide

Ion	Limit, [Ion] / [As]		Ion	Limit, [Ion] / [As]	
	$NaBH_4$ red.[a]	$NaBH_4$/KI red.		$NaBH_4$ red.	$NaBH_4$/KI red.
V^{5+}	1000	2000	Cu^{2+}	200	2000
Bi^{3+}	400	400	Sb^{3+}	60	60
Te^{4+}	400	800	Sn^{4+}	60	60
Ni^{2+}	400	800	Se^{4+}	10	2000

The following are tolerable: Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-, SiO_3^{2-} (excess, x 20000), Sr^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}, Cr^{3+}, Cr^{6+}, Mo^{6+}, Co^{2+}, Pb^{2+}, Hg^{2+}, Se^{6+}, PO_4^{3-} (excess, x 2000).

Solution contained 0.5 μg of As(III) and 10mg of Fe(III); volume, 500m*l*.

[a] $NaBH_4$ reduction.

a gas-collection method eliminated interferences from many diverse ions. In the procedure described here potassium iodide pretreatment eliminated suppressive effects by copper(II), nickel(II) and selenium(IV), but did not have much effect on negative interferences arising from the presence of antimony(III) and tin (IV). In general, the quantities of these ions in uncontaminated sea water are low compared with arsenic content. Thus, this method is not affected by various ions existing in natural sea water.

Analyses were also carried out on 250–m*l* sample of clear uncontaminated sea water, filtered through a Millipore filter HA (pore size 0.45 μm) after addition of 10 m*l* of hydrochloric acid per 1000 m*l* of sample, immediately after collection.

Table 2 presents recovery data on arsenic(III, V) added to natural sea water samples by the above procedure. The mean overall recovery was 101 and 99 % for arsenic(III) and arsenic(V), respectively. The arsenic concentrations of seashore sea water collected at Shibukawa, Okayama Prefecture, are shown in Table 3. The relative standard deviations of seven replicate analyses

TABLE 2
Recovery of arsenic added to sea water

Sample taken (m*l*)	Arsenic added (μg)	Arsenic [c] found (μg)	Arsenic recovered (μg)	Recovery (%)
250	None	0.396±0.009		
250	0.300 [a]	0.699±0.012	0.303	101
250	0.300 [b]	0.692±0.016	0.296	99

This sample was collected on March 17th, 1978 at Shibukawa, Okayama Prefecture.
[a] Added as arsenite.
[b] Added as arsenate.
[c] Mean ± SD of seven measurements.

TABLE 3
Arsenic content in sea water sample in 1978

Dete of collection [a]	Arsenic content in sea water [b] ($\mu g\ l^{-1}$)
March 17	1.58±0.04
May 15	1.57±0.03
July 15	1.45±0.02
July 18	1.51±0.02
August 8	1.62±0.04
August 24	1.60±0.04
	1.61±0.04 [c]

[a] These samples were taken at Shibukawa, Okayama Prefecture.
[b] Mean ± SD of seven measurements.
[c] Coprecipitation and flotation at pH 4–5 using sodium lauryl sulfate.

of 250–m*l* sea water samples varied less than 3 %.

This method offers a simple, rapid and precise procedure for routine determinations of arsenic in natural sea water.

SUMMARY

A rapid and precise method is described for separation and determination of arsenic in natural sea water. A sub-microgram amount of arsenic(III, V) in a 250–m*l* sample of sea water is coprecipitated with iron(III) hydroxide at pH 8–9. The precipitate is floated with the aid of sodium oleate and small air bubbles, then separated and dissolved in 5 M hydrochloric acid. The arsenic content is determined by generation of arsine using sodium borohydride as a reductant and atomic-absorption spectrophotometry with a long absorption cell (60 × 1.2 cm i.d.). Potassium iodide pretreatment after the separation eliminates the suppressive effects by various ions, such as copper(II), selenium(IV) and nickel(II). In the analytical process, mean recovery was 99–101 % for arsenic(III, V) added to natural sea waters. The relative standard deviations of seven replicate sea water samples did not vary by more than 3 %.

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LITERATURE CITED

1. Sugawara, K., Terada, K., Kanamori, S. and Okabe, S. 1962. On different distribution of calcium, strontium, iodine, arsenic and molybdenum in the northwestern Pacific, Indian and Antarctic Oceans. J. Earth. Sci., Nagoya Univ. 10: 34 – 50.
2. Portmann, J. E. and Riley, J. P. 1964. Determination of arsenic in sea water, marine plants and silicate and carbonate sediments. Anal. Chim. Acta. 31: 509 – 519.
3. Johnson, D. L. and Pilson, M. E. Q. 1972. Arsenate in the Western North Atlantic and adjacent regions. J. Mar. Res. 30: 140–149.
4. Ferguson, J. F. and Gavis, J. 1972. A review of the arsenic cycle in natural waters. Water Res. 6: 1259 – 1274.
5. Yamamoto, Y., Kumamaru, T., Hayashi, Y. and Kamada, T. 1973. Atomic absorptiometric determination of ppb levels of arsenic in water by arsine-argon•hydrogen flame system combined with use of zinc powder tablets, potassium iodide and stannous choride as reductant. Bunseki Kagaku. 22: 876 – 881.
6. Yamamoto, Y., Kumamaru, T., Edo, T. and Takemoto, J. 1976. Atomic absorptiometric determination of ppb levels of arsenic in water by arsine-nitrogen•hydrogen flame system combined with use of sodium borohydride tablet and potassium iodide. Bunseki Kagaku. 25: 770 – 775.
7. Thompson, K. C. and Thomerson, D. R. 1974. Atomic-absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by utilising the generation of covalent hydrides. Analyst (London). 99: 595 – 601.

8. Goulden, P. D. and Brooksbank, P. 1974. Automated atomic absorption determination of arsenic, antimony, and selenium in natural water. Anal. Chem. 46: 1431 – 1436.
9. Sugawara, K., Tanaka, M. and Kanamori, S. 1956. Spectrophotometric microdetermination of arsenic in natural waters and its application to silicate and biological materials. Bull. Chem. Soc. Jpn. 29: 670 – 673.
10. Nakashima, S. 1978. Flotation of sub-microgram amounts of arsenic coprecipitated with iron(III) hydroxide from natural waters and determination of arsenic by atomic-absorption spectrophotometry following hydride generation. Analyst (London). 103: 1031 – 1036.
11. Hiraide, M. and Mizuike, A. 1977. Flotation of iron(III) hydroxide precipitate. Bunseki Kagaku. 26: 47–50
12. Hiraide, M., Yoshida, Y. and Mizuike, A. 1976. Flotation of traces of heavy metals coprecipitated with aluminum hydroxide from water and sea water. Anal. Chim. Acta. 81: 185 – 189.
13. Lyman, J. and Fleming, R. H. 1940. Composition of sea water. J. Mar. Res. 3: 134 – 146.
14. Yamamoto, Y. and Kumamaru, T. 1976. Masking effect of potassium iodide on interferences in the determination of arsenic *via* the hydride by atomic-absorption spectrophotometry using the sodium borohydride tablet as the reductant. Z. Anal. Chem. 282: 139.